Formation and decay of the peroxy radicals in the oxidation process of Glyoxal, Methylglyoxal and Hydroxyacetone in aqueous solution

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Motivation

- Large amounts of volatile organic compounds (VOCs) emitted into the atmosphere from biogenic and anthropogenic sources

- Further oxidation of emitted VOCs in gas phase and aqueous phase (cloud droplets, fog, rain and deliquescent particles) to semivolatile carbonyl compounds

- Carbonyl compounds such as glyoxal and methylglyoxal from isoprene oxidation processes, hydroxyacetone from biomass burning

- Semivolatile carbonyl compounds important for formation of secondary organic aerosol (SOA) by partitioning between gas- and liquid phase of pre-existing particles

- Initiation of oxidation process by radicals (OH and NO_3) under formation of peroxy radicals and substituted organics

- Oxidation pathways of glyoxal after H-atom abstraction still uncertain

- Buxton et al., 1997 (dilute solutions < 1 mM, typical concentration for cloud water) peroxy radical formation with a rate constant of k = 1 × 10^9 M^{-1} s^{-1}

- Lim et al., 2010 (concentrations > 1 mM) formation of peroxy radicals minor important because of lower rate constant of k = 1 × 10^6 M^{-1} s^{-1} estimated after Guzman et al., 2006
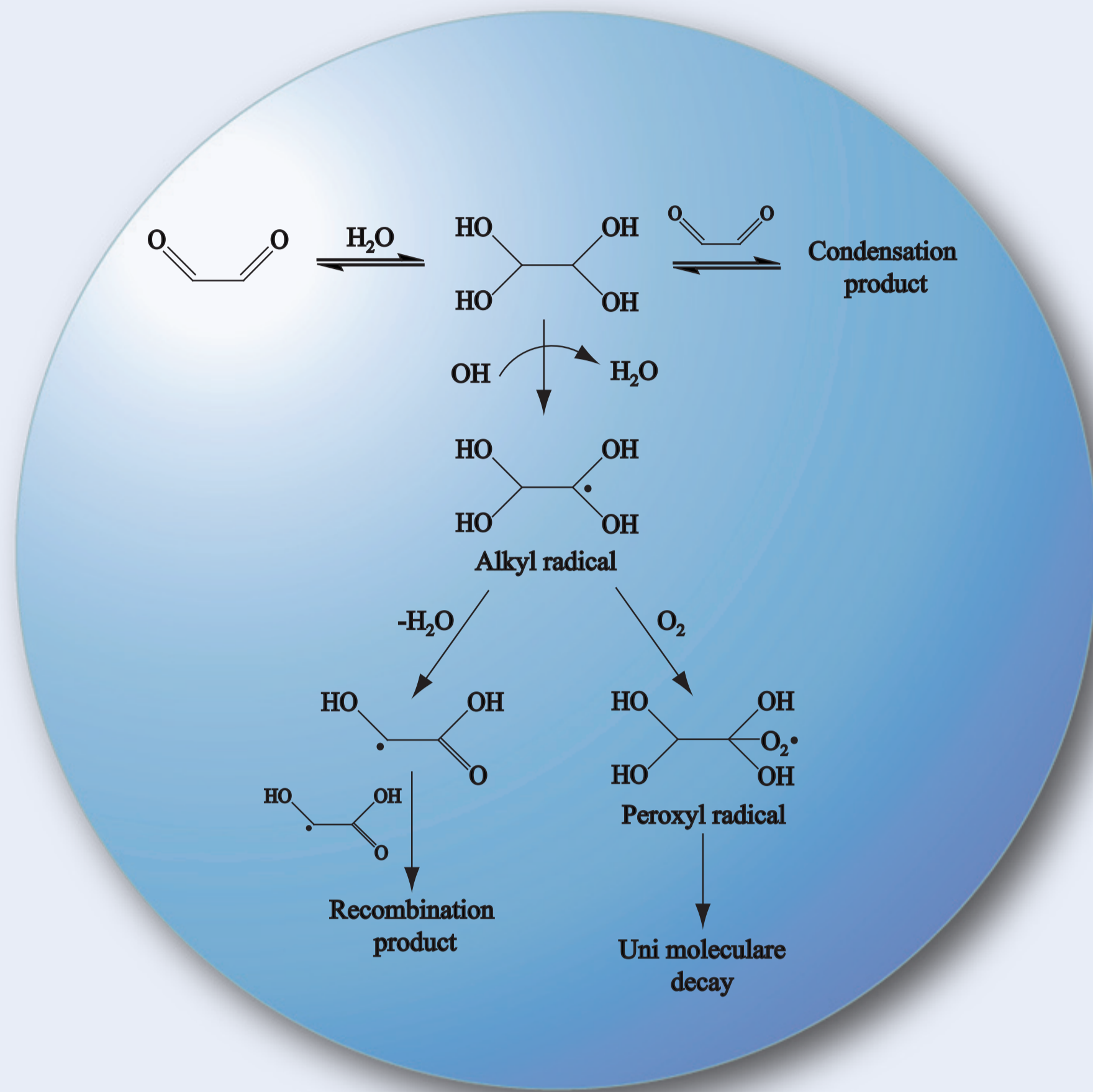

Figure 1: Glyoxal oxidation by OH radicals in aqueous solution.

Methods

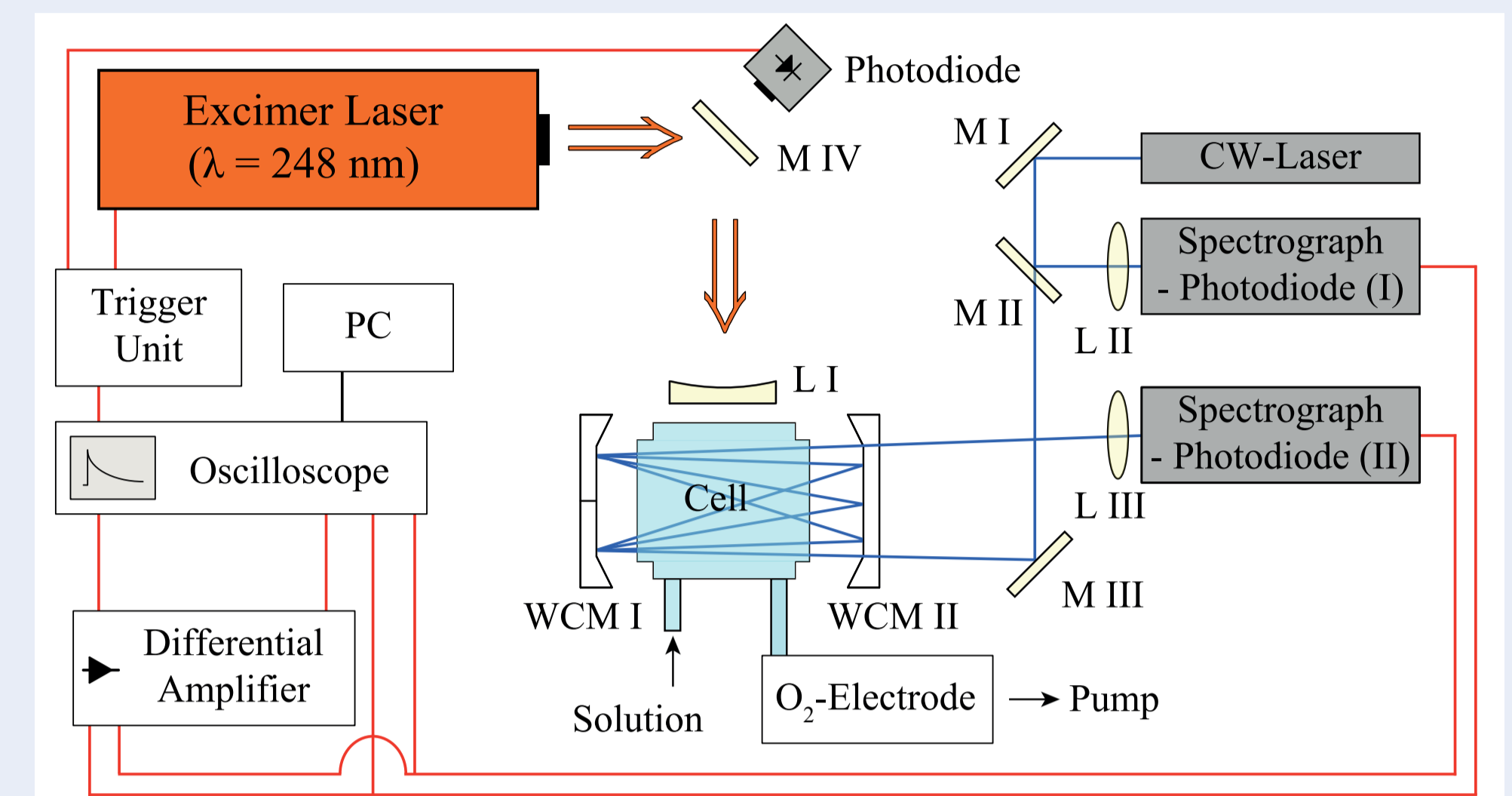- Investigation of formation and decay with Laser Photolysis Long Path Absorption (LP-LPA) setup (Figure 2)

Figure 2: Laser Photolysis Long Path Absorption setup (LP-LPA).

- OH radicals production by laser flash photolysis of hydrogen peroxide (H_2O_2)

- Determination of initial OH radical concentration using thiocyanate (SCN^-) as OH scavanger,

  molar absorption coefficients $\varepsilon(SCN^-) = 60 \pm 3$ M^{-1} cm^{-1}
  molar absorption coefficients $\varepsilon(H_2O_2) = 25.65 \pm 1$ M^{-1} cm^{-1},
  quantum yield $\Phi_{248\,nm}(H_2O_2) = 1.02 \pm 0.1$ (Herrmann et al, 2010)
  reference constant $k_{(OH+SCN^-)} = 1.24 \times 10^{10}$ M^{-1} s^{-1} (Chin and Wine, 1994)

- Analyical light sources: λ = 325 nm HeCd laser
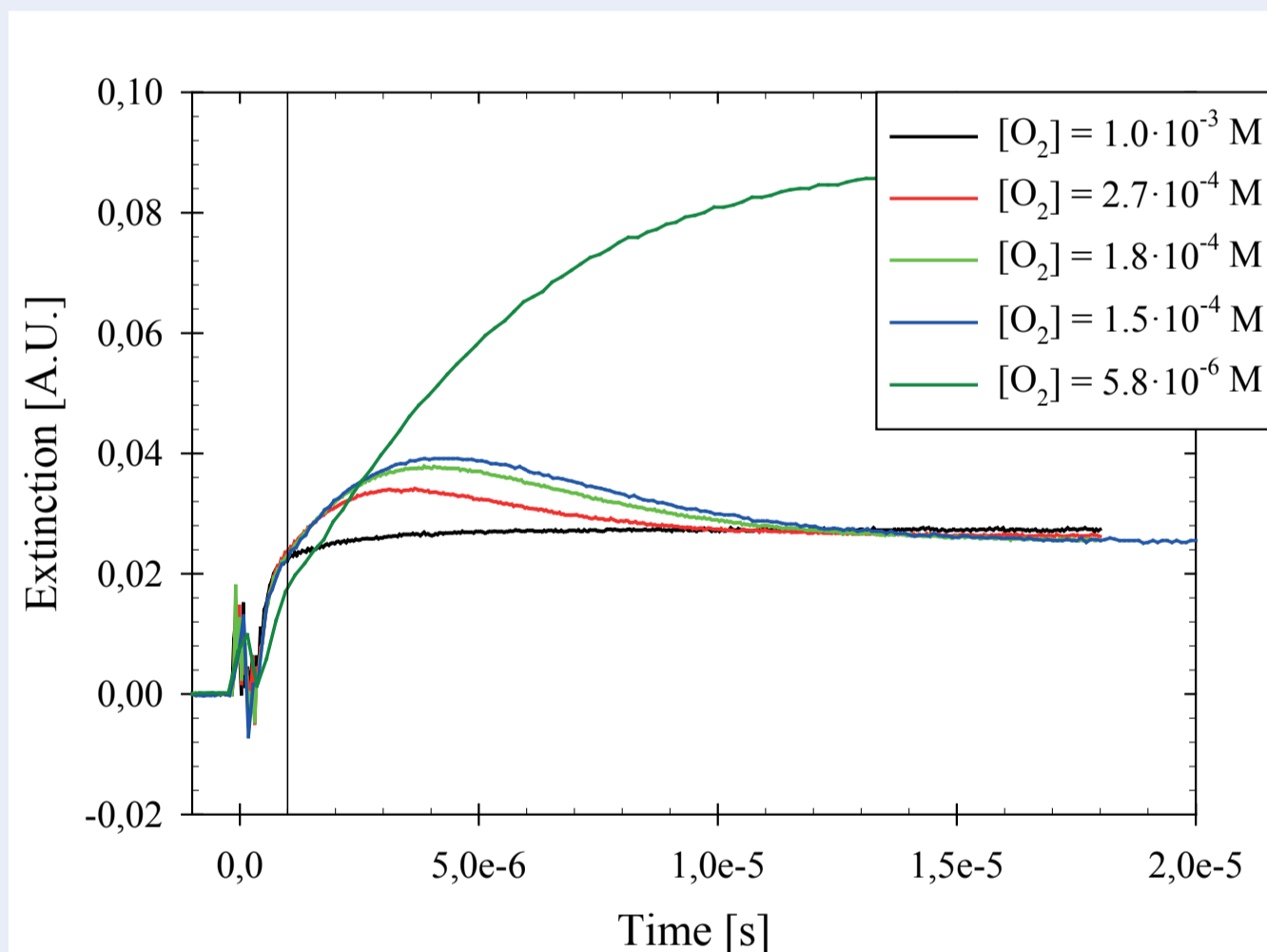 λ = 244 nm frequency doubled Ar ion laser

Results

O_2 measurement

Figure 3: Absorption traces of glyoxal oxidation by OH radicals (T = 298 K, pH = 2 [H_2O_2] = 2·10^{-4} M, [Glyoxal] = 5·10^{-4} M).

- Determination of lower rate constant (experimental data raw analysis (Figure 3)) of O_2 addition to glyoxyl radical with k(R· + O_2) ≥ (1.2 ± 0.2)·10^8 $M^{-1}s^{-1}$

- Model mechanism includes reactions of HO_x-radicals, of acid-base equilibriums, alkyl and peroxy radicals

- Model results of high O_2 conditions in table 1

- Unimolecular decay of glyoxylperoxy radical considering the absorption of HO_2 radicals (k_{1st} = 122 s^{-1})

- Under low O_2 conditions isomerization of glyoxyl radical to glycolic acid radical (k_{1st} = 1,8·10^5 s^{-1})

- Modelled extinction coefficient $\varepsilon_{244\,nm}$(glycolic acid radical) = 3070 $M^{-1}cm^{-1}$

Table 1: Modelled results and literature comparison.

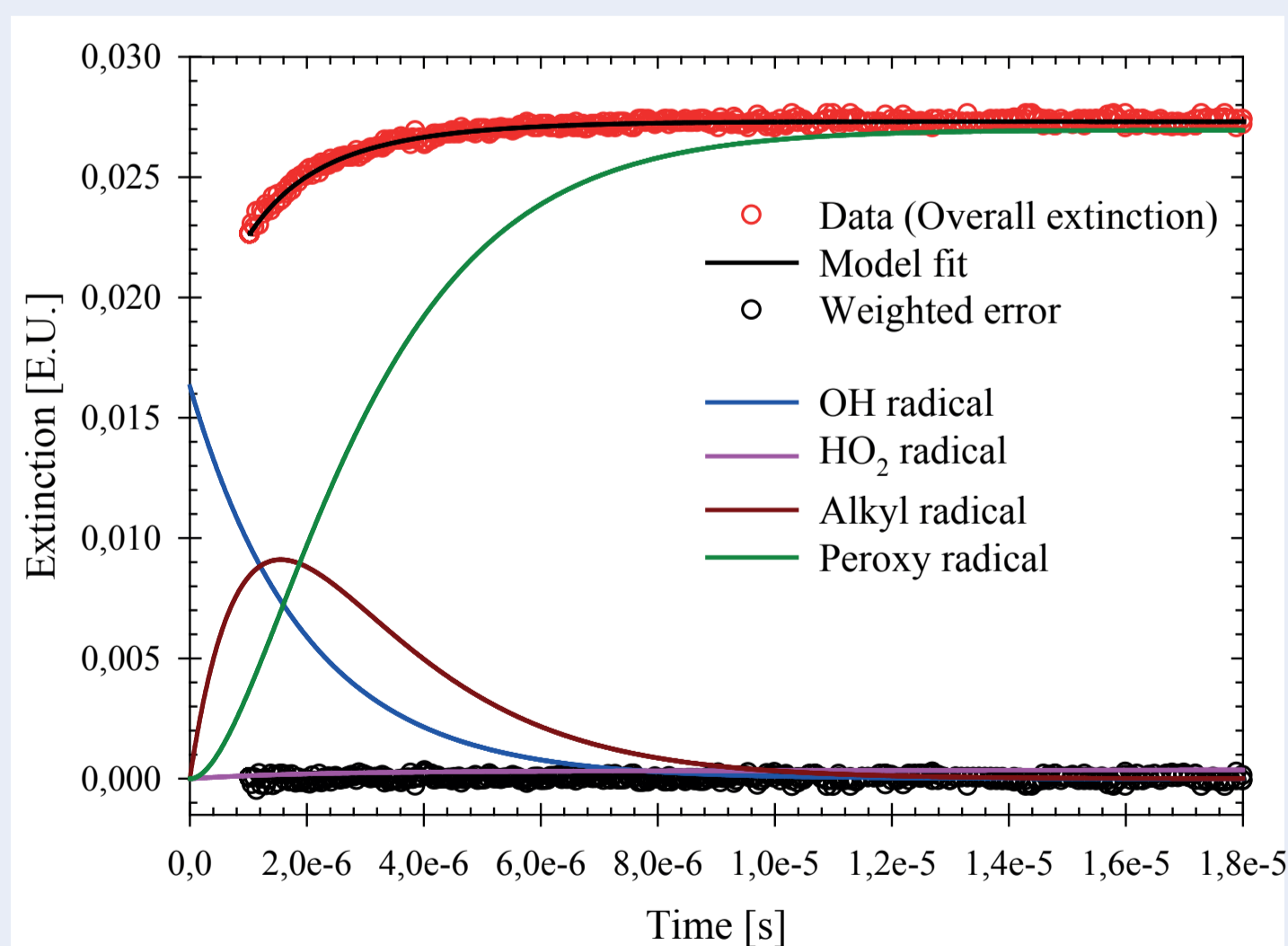| T [K]	k(R· + O_2) [$M^{-1}s^{-1}$]	$\varepsilon_{244\,nm}$ (R·) [$M^{-1}cm^{-1}$]	$\varepsilon_{244\,nm}$ (RO$_2$·) [$M^{-1}cm^{-1}$]	Reference
298	(1,2 ± 0,3)·10^9	1168	892	This work
293	(1,38 ± 0,11)·10^9	1105	941	Buxton et al., 1997

Figure 4: Modelled absorption traces in O_2 saturated aqueous solution.
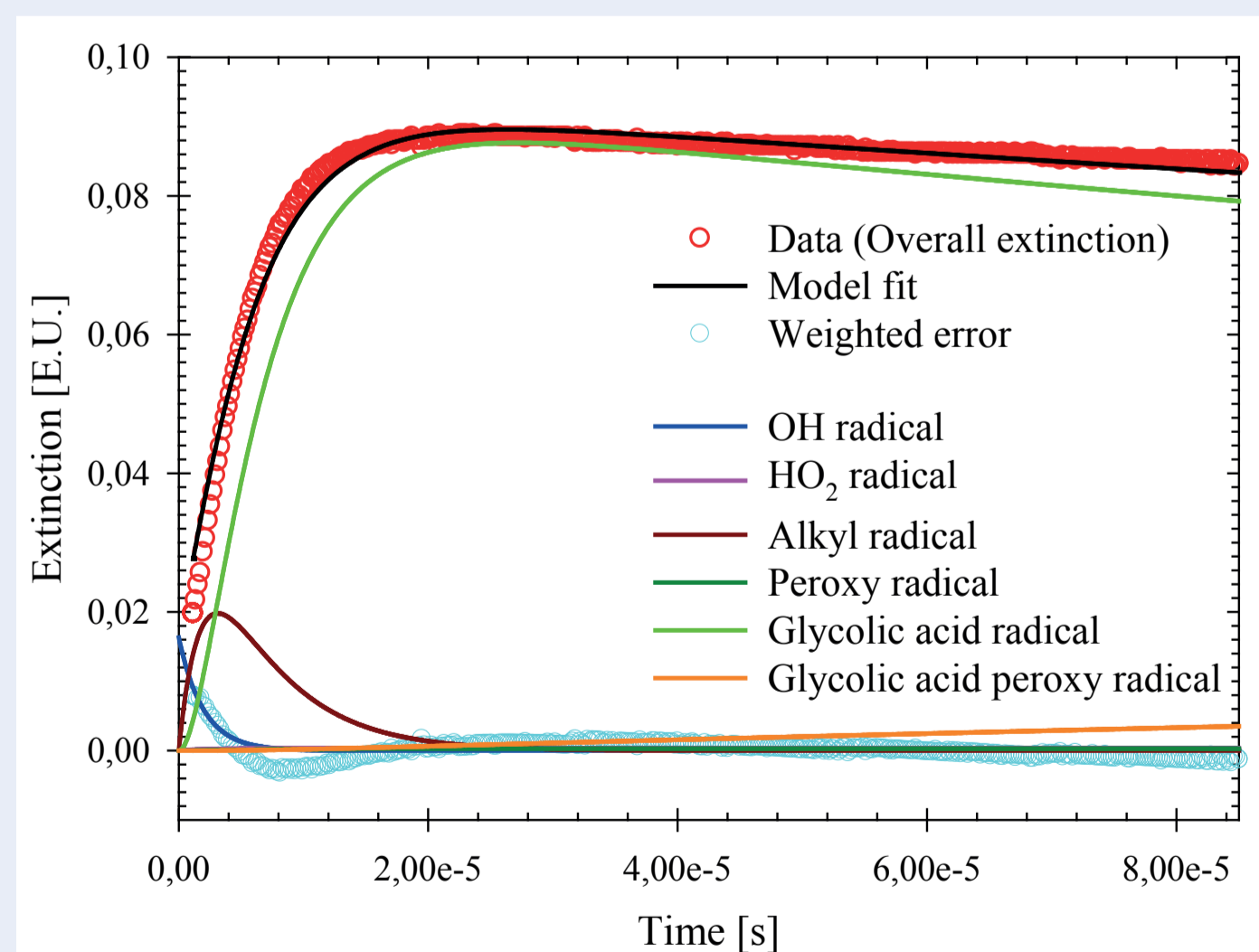

Figure 5: Modelled absorption traces under low O_2 concentration.
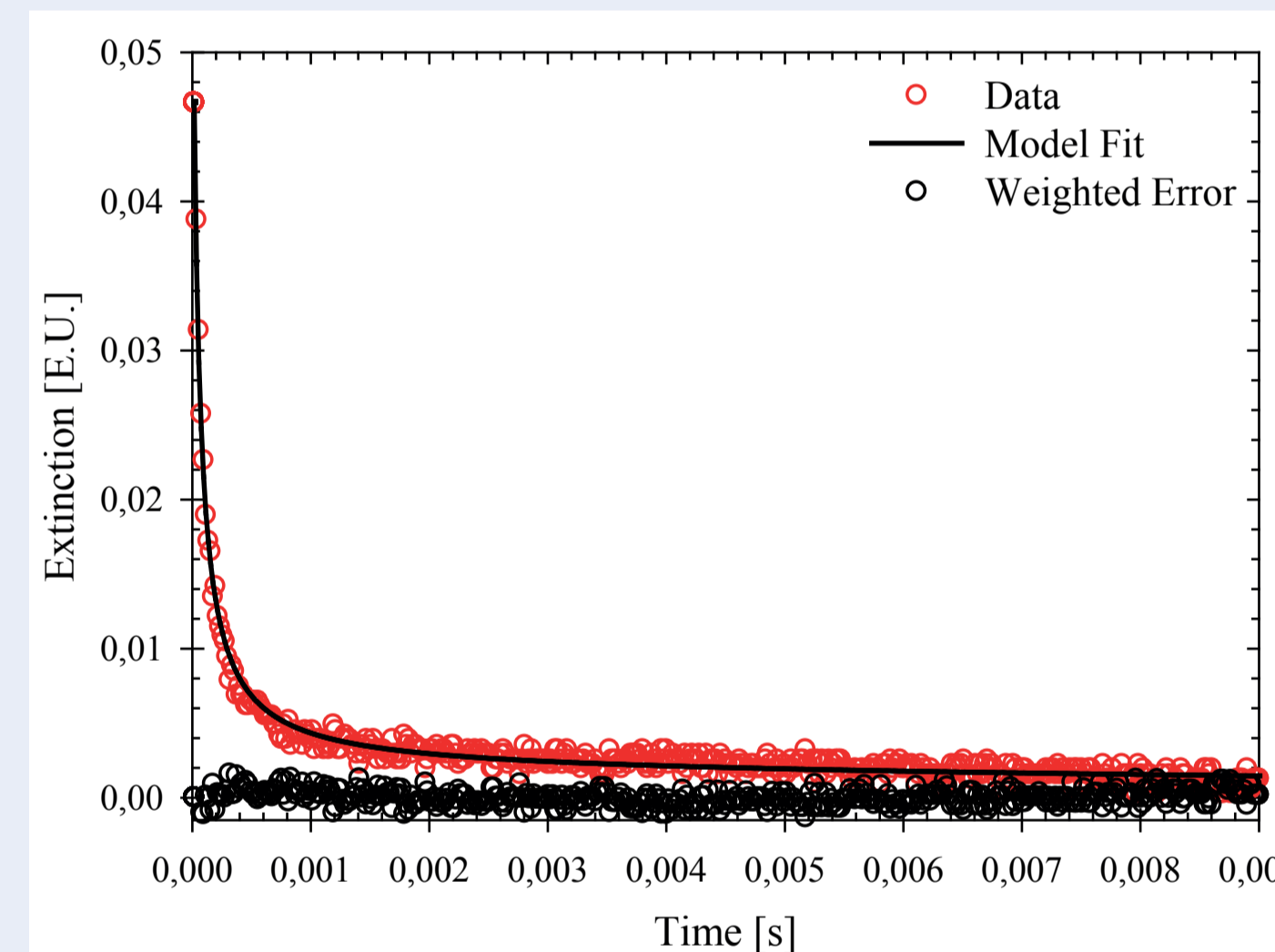
Recombination of peroxy radical

Figure 6: Absorption traces of Hydroxyacetone oxidation by OH radicals (T = 298 K, pH = 2, [H_2O_2] = 2·10^{-3} M, [HyAce] = 1·10^{-3} M).

- Recombination observed of peroxy radicals instead of proposed unimolecular HO_2 radical elimination

Decay of peroxy radical modelled by using simplified model mechanism
$RO_2 \longrightarrow$ Product
Product $\longrightarrow$ Secondary Product

Table 2: Results of hydroxyacetonyl peroxy radical recombination

$\varepsilon_{325\,nm}$ [$M^{-1}cm^{-1}$]	$k_{298\,K}$ [$M^{-1}s^{-1}$]	E_A [kJ mol^{-1}]	A [$M^{-1}s^{-1}$]	Method
254	(1,9 ± 0,1)·10^9	18 ± 21	(2,7 ± 0,8)·10^{12}	Simple model
254	(1,9 ± 0,1)·10^9	18 ± 12	(2,2 ± 0,4)·10^{12}	Classical evaluation

Table 3: Results of methylglyoxyl peroxy radical recombination

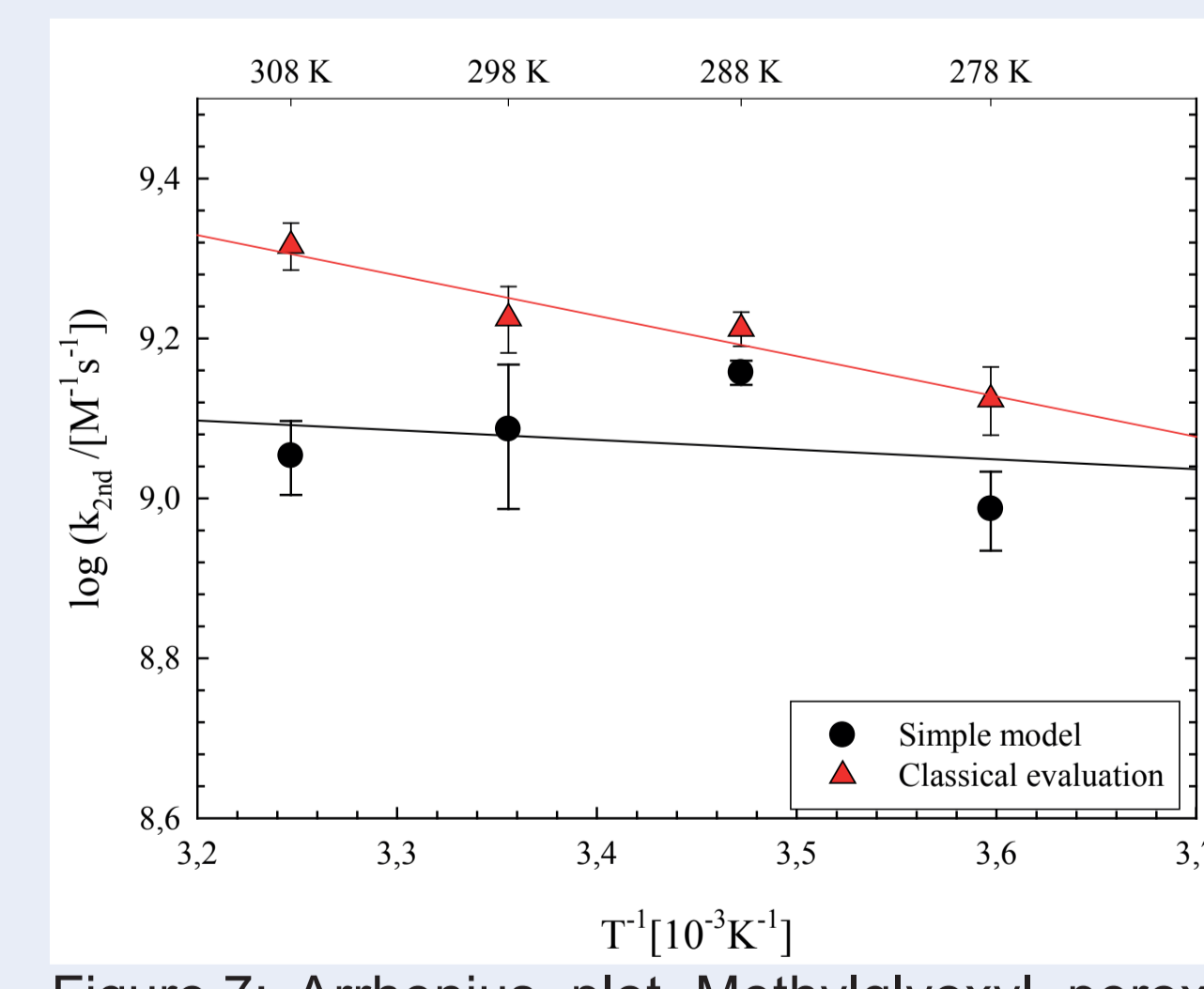| $\varepsilon_{325\,nm}$ [$M^{-1}cm^{-1}$]	$k_{298\,K}$ [$M^{-1}s^{-1}$]	E_A [kJ mol^{-1}]	A [$M^{-1}s^{-1}$]	Method
182	(1,2 ± 0,3)·10^9	2,3 ± 16,1	(2,5 ± 0,8)·10^9	Simple model
182	(1,7 ± 0,2)·10^9	9,7 ± 4,7	(7,3 ± 0,6)·10^{10}	Classical evaluation

Figure 7: Arrhenius plot Methylglyoxyl peroxy radical recombination.
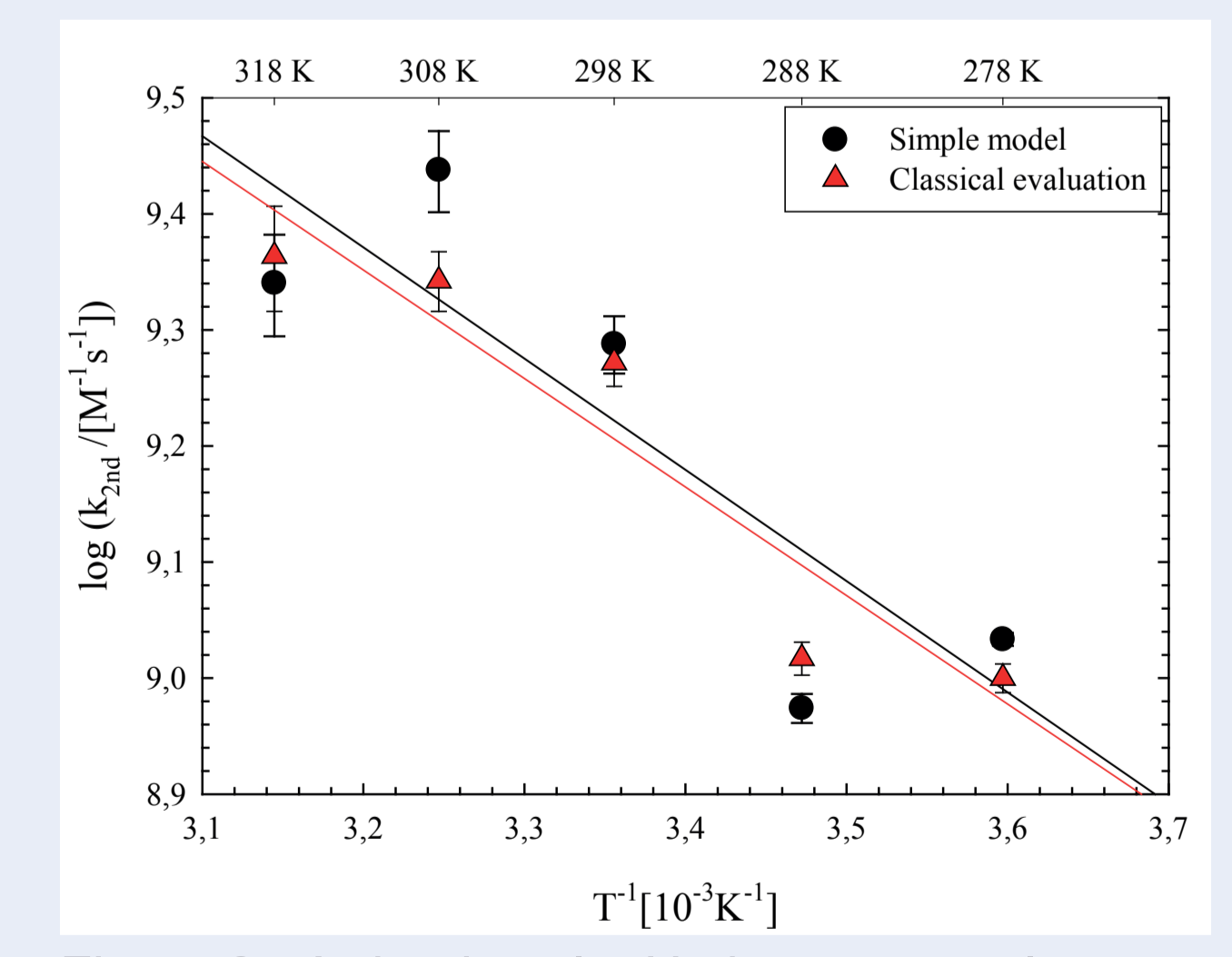

Figure 8: Arrhenius plot Hydroxyacetonyl peroxy radical recombination.

Conclusions, Outlook and Literature

Conclusions

- O_2 dependent measurements from glyoxal oxidation

- Determination of lower rate constant (experimental data raw analysis) of O_2 addition to glyoxyl radical with k(R· + O_2) ≥ (1.2 ± 0.2)·10^8 $M^{-1}s^{-1}$

- Modelled rate constant (experimental data fit) for O_2 addition: k(R· + O_2) = 1 × 10^9 $M^{-1}s^{-1}$

  ↳ Fast O_2 addition to alkyl radical from glyoxal oxidation! (confirmed by this work and Buxton et al., 1997)

- T-dependencies for hydroxyacetonyl peroxy and methylglyoxyl peroxy radical for recombination

- Recombination observed at high RO_2 radical concentrations instead of unimolecular HO_2 radical elimination

Outlook

- Measurements of glycolic acid oxidation in dependence on O_2 concentration

- Determination of extinction coefficient of glycolic acid alkyl radical and glycolic acid peroxy radical

- Concentration dependencies for recombination reaction of hydroxyacetonyl peroxy and methylglyoxyl peroxy radical

Literature

Buxton et al., J. Chem. Soc. Faraday Trans., 1997, 93, 2889–2891. Chin and Wine in Aquatic and Surface Photochemistry (Eds. Helz, Zepp, Crosby), Lewis Publishers, Boca Raton, 1994, 85–96. Guzman et al., J. Phys. Chem. A, 2006, 110, 3619–3626. Herrmann et al., ChemPhysChem, 2010, 11, 3796-3822. Lim et al., Atmos. Chem. Phys., 2010, 10, 10521-10539.